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(71)Applicant : TONEN CORP

SEKIYU SANGYO KASSEIKA
CENTER

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(72)Inventor : ANDOU MOTOAKI

KOIDE HIDETO

SOMEYA YOSHIYUKI

MUKAISAWA ISAO

YOSHIDA TOSHIHIKO

(54) SOLID ELECTROLYTE FUEL CELL ANODE AND SOLID ELECTROLYTE FUEL CELL USING IT, AND SOLID ELECTROLYTE FUEL CELL OPERATING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To sufficiently control temperature distribution within a cell surface, and stably maintain cell performance for a long time by using a material showing a catalytic action of reforming reaction of fuel gas and specifying the specific surface area of the material on the surface part coming in contact with the fuel gas of an anode.

SOLUTION: In a solid electrolyte fuel cell anode, the surface part at least coming in contact with fuel gas is made of a material such as cermet showing catalytic action of reforming reaction of the fuel gas. On the surface part of the anode, the specific surface area of the material is made larger in a portion on fuel gas outlet side than a portion on the fuel gas inlet side. The surface area is selected preferably from the range of 0.01-0.2m²/g in the portion on the fuel gas inlet side, and from the range of 0.5-2.0m²/g in the portion on the fuel gas outlet side. Attaching of the anode to a solid electrolyte is conducted by screen printing or brush coating.

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CLAIMS

[Claim(s)]

[Claim 1] The anode for solid oxide fuel cells characterized by using what showed the catalysis of the reforming reaction of fuel gas as the ingredient about the surface section in the anode for solid oxide fuel cells which contacts fuel gas at least, and made the part of a fuel gas outlet side larger than the part of a fuel gas entrance side about the specific surface area.

[Claim 2] The solid oxide fuel cell characterized by using an anode according to claim 1 as an anode in the solid oxide fuel cell which is equipped with two sorts of external terminals which established each material gas path in the cell and one side which prepared the cathode and the anode in both sides of a solid electrolyte, respectively, accumulates these, and changes.

[Claim 3] The solid oxide fuel cell characterized by using an anode according to claim 1 as an anode in the solid oxide fuel cell which is equipped with the external terminal which prepared each material gas path at the vertical end of the direction of a laminating of a unit cell at the unit cell which prepared the cathode and the anode in both sides of a solid electrolyte, respectively, the separator which prepared each material gas path in the crossover direction mutually to both sides, respectively, and one side, accumulates these, and changes.

[Claim 4] The operating method of the solid oxide fuel cell according to claim 2 or 3 characterized by supplying this to a fuel gas path equally with a steam, using a hydrocarbon as fuel gas.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention improves the variation in the temperature distribution in the field of a solid oxide fuel cell, and relates to the operating method of the solid oxide fuel cell and this cell using the anode for solid oxide fuel cells, and it which can maintain a battery life for a long period of time.

[0002]

[Description of the Prior Art] In the fuel cell, hydrocarbons, such as methane, are used for

fuel gas, fuel gas was transformed to hydrogen etc. by reforming reactions, such as steam reforming, and although using this as substantial fuel gas was performed widely, the fuel cells including such a thing generally enlarged had the problem that the vertical width of face of the temperature distribution within a cel side was large. That is, although it sets at the time of actuation of a fuel cell and fuel gas is usually equally supplied and distributed to a part for each feed zone of a cel, if the temperature distribution within a cel side are seen about the passage of fuel gas in that case, the direction of an entry side will be [the direction of low temperature and an outlet side] an elevated temperature, and, moreover, near the intersection of the outlet approach of each passage of oxidizer gas, such as fuel gas and air, will serve as the maximum elevated temperature. For the variation in such temperature distribution, in the low-temperature section, cell performance degradation arises, it becomes difficult to maintain a battery life for a long period of time that corrosion etc. tends to advance in the elevated-temperature section, especially it becomes a serious problem at the thing of large-scale stack structure. For this reason, although measures, such as inserting a refrigeration unit for every number cel, were made, member mark increased and it did not escape becoming cost quantity.

[0003] For this reason, in the thing of an internal reforming type, control of the temperature distribution within a cel side is directly performed by the fused carbonate fuel cell, optimizing the pack density of a reforming catalyst, etc. above all. Generally a fused carbonate fuel cell directly [this] the thing of an internal reforming type with the reforming method of the fuel supplied to it Although it is divided roughly into the external reforming method which prepares a reformer apart from the body of a fuel cell, and the internal reforming method which reforms a fuel inside a cell and especially the latter is excellent in respect of the miniaturization of a system, improvement in generating efficiency, etc. It is the thing of the method which arranges a reforming catalyst in the fuel gas path of the body of a fuel cell by which promising ** is carried out in this internal reforming method.

[0004] On the other hand, in a solid oxide fuel cell, a reforming catalyst is not arranged apart from an electrode material like said fused carbonate fuel cell, but an anode acts as a reforming catalyst as it is, and a reforming reaction occurs on the anode front face which mainly touches fuel gas with a quick reaction rate. For this reason, since this reaction was endothermic reaction when a reforming reaction inclines and occurs in a fuel gas passage entry side and it uses a steam-reforming reaction especially, the rapid temperature fall was caused in the cel side by the side of a fuel gas passage entry, it did not escape that the temperature distribution within a cel side were expanded further, but further, since distortion by thermal stress occurred in an ununiformity, control of these temperature distribution was demanded strongly.

[0005]

[Problem(s) to be Solved by the Invention] This invention improves the variation in temperature distribution under such a situation, and it is made for the purpose of offering the operating method of the predetermined solid oxide fuel cell which used this anode

effectively, and this cell while offering the anode for solid oxide fuel cells which can maintain a battery life for a long period of time.

[0006]

[Means for Solving the Problem] that the anode for solid oxide fuel cells which has said desirable property carried out should be developed, this invention persons consist of ceramics which does not show the catalysis of a reforming reaction to the part of a fuel gas entrance side among the contact surfaces with the fuel gas of the anode which has reforming catalyst ability previously, as a result of repeating research wholeheartedly -- given thickness -- the anode for predetermined fuel cells which prepared the gas permeability porous layer of a predetermined aperture was proposed (Japanese Patent Application No. No. 92500 [seven to]). Without concentrating and biasing reforming reactions, such as a steam-reforming reaction, toward a fuel gas entrance side, from it, open this anode also to the downstream, it is made to perform, shifts the core of the part from which a reforming reaction occurs to the downstream, and controls the temperature distribution within a cel side. Without preparing another enveloping layer, in order that this invention persons may not bias a reaction part like this anode, as a result of repeating research further It forms also in an anode ingredient with reforming catalyst ability only with these anode ingredients, such as a homogeneous material, for example, the cermet of a homogeneity presentation etc. And by [of an anode] making the fuel gas outlet side at least larger than the fuel gas entrance side about the specific surface area of the contact surface section with fuel gas In the cel using this anode, the temperature distribution within a cel side can be enough controlled over a long period of time, and it came to make this invention for the ability of the cel engine performance to be maintained to stability for a long period of time based on a header and this knowledge.

[0007] Namely, this invention (1) About the surface section in the anode for solid oxide fuel cells which contacts fuel gas at least The anode for solid oxide fuel cells characterized by using what showed the catalysis of the reforming reaction of fuel gas as the ingredient, and made the part of a fuel gas outlet side larger than the part of a fuel gas entrance side about the specific surface area, (2) In the solid oxide fuel cell which is equipped with two sorts of external terminals which established each material gas path in the cel and one side which prepared the cathode and the anode in both sides of a solid electrolyte, respectively, accumulates these, and changes The solid oxide fuel cell characterized by using an anode given [aforementioned] in (1) term as an anode, (3) The unit cell which prepared the cathode and the anode in both sides of a solid electrolyte, respectively, In the solid oxide fuel cell which is equipped with the external terminal which established each material gas path in both sides at the vertical end of the direction of a laminating of a unit cell at the separator and one side which prepared each material gas path in the crossover direction mutually, respectively, accumulates these, and changes The solid oxide fuel cell characterized by using an anode given [aforementioned] in (1) term as an anode, and (4) As fuel gas The operating method of a solid oxide fuel cell the aforementioned (2) term characterized by supplying this to a fuel gas path equally with a steam or given in (3)

terms is offered using a hydrocarbon. As the desirable mode (5) of this invention The anode given [aforementioned] in (1) term with which the anode was chosen from the cermet of nickel, nickel oxide and nickel, and the ceramics and which is at least one sort, (6) Specific surface area in the part of a fuel gas entrance side 0.01-0.2m²/g, The anode given [aforementioned] in (1) term which is 0.5-2.0m²/g in the part of a fuel gas outlet side, (7) The ceramics A zirconia, fully stabilized zirconia, Seria, an alumina -- silicon nitride -- and -- in addition to this -- oxygen tension -- one -- x -- ten - 20 -- atm -- an ambient atmosphere -- the bottom -- 1200 -- degree C -- not fusing -- the ceramics -- inside -- from -- choosing -- having had -- at least -- one -- a sort -- it is -- the above -- (-- five --) -- a term -- or -- (-- six --) -- a term -- a publication -- an anode -- (8) The aforementioned (5) term whose cermet is the cermet of nickel and a zirconia, or nickel and the cermet of Seria, (6) A term or anode given in (7) terms (9) The unit cell which prepared the anode which has a cathode and reforming catalyst ability in both sides of a solid electrolyte, respectively, In the solid oxide fuel cell which is equipped with the external terminal which established each material gas path in both sides like each material gas path of a separator at the separator and one side which prepared each material gas path in the crossover direction mutually, respectively, accumulates these, and changes Solid oxide fuel cell ** characterized by using the anode of a publication for either the aforementioned (5) term thru/or (8) terms as an anode is mentioned. as the mode of the most desirable anode -- (10) an anode -- a solid electrolyte -- an interface -- the neighborhood -- an anode -- a part -- 0.5 - 2.0 -- m -- two -- /-- g -- it is -- specific surface area -- having -- the above -- (-- one --) -- a term -- (-- five --) -- a term -- (-- six --) -- a term -- (-- seven --) -- a term -- and -- (-- eight --) -- a term -- either -- a publication -- an anode -- ** -- mentioning -- having .

[0008] In the anode of this invention, not only this surface section but the whole anode consists of the surface section which contacts fuel gas at least, and an ingredient in which the catalysis of the reforming reaction of fuel gas is shown preferably. As for this ingredient, it is desirable that it is a homogeneous material, for example, the cermet of a homogeneity presentation etc.

[0009] About this anode ingredient, although it will not be restricted especially if it has fuel gas, especially the thing which shows the catalysis of the reforming reaction of a hydrocarbon, i.e., reforming catalyst ability, at least one etc. sort chosen from the cermet of what shows the catalysis of the reforming reaction of hydrocarbons, such as methane, ethane, a propane, butane, and LNG, especially a steam-reforming reaction preferably, for example, nickel, nickel oxide and nickel, and the ceramics is mentioned.

[0010] As ceramics which constitutes the above-mentioned cermet, the ceramics which is not fused at 1200 degrees C under fully stabilized zirconia, such as a zirconia and yttria stabilized zirconia (henceforth YSZ), Seria, an alumina, silicon nitride, and the other ambient atmospheres of oxygen tension 1x10⁻²⁰atm is mentioned.

[0011] As the above-mentioned cermet, they are nickel-zirconia, nickel oxide-zirconia, and nickel-Seria, nickel oxide-Seria, nickel-YSZ, and nickel oxide preferably. · YSZ is mentioned.

[0012] About said surface section of the anode of this invention, the specific surface area of the ingredient needs to enlarge the part of a fuel gas outlet side than the part of a fuel gas entrance side. this specific surface area -- the part of a fuel gas entrance side -- setting -- desirable -- $0.01\text{--}0.2\text{m}^2/\text{g}$ -- more -- desirable -- the part of $0.01\text{--}0.1\text{m}^2/\text{g}$ and a fuel gas outlet side -- setting -- desirable -- $0.5\text{--}2.0\text{m}^2/\text{g}$ -- it is more preferably chosen in the range of $0.5\text{--}1.0\text{m}^2/\text{g}$. Moreover, although what bisected this surface section into the suitable ratio, every [for example, $2/1$], for example, and was changed as mentioned above about the specific surface area of that ingredient as a gestalt of the anode of this invention by part for a part for the fuel gas entrance side of one of these and the fuel gas outlet side of another side is mentioned While bisecting not only the surface section but the whole anode into a suitable ratio and considering as a monolayer about a part for the fuel gas outlet side preferably It is good to compare with the completely same lower layer and the completely same it as a part for two-layer structure, for example, a fuel gas outlet side, about a part for a fuel gas entrance side, and for specific surface area to consider as a laminated structure with the small upper layer etc. Moreover, since electrode activity ***** influences polarization resistance etc. directly in the amount of the specific surface area in the anode part near the interface of an anode and a solid electrolyte, and the part which touches the solid electrolyte of an anode especially, Although the larger one of this specific surface area is desirable, as the whole cell which incorporated the whole anode with other members Since the cel engine performance which was excellent in comprehensive balance, such as output density, the good cel engine performance, i.e., the conversion efficiency, of balance, endurance, and stability, on the whole is required, the range of $0.5\text{--}2.0\text{m}^2/\text{g}$ is suitable as this specific surface area.

[0013] As the covering approach to the solid electrolyte of the anode of this invention, screen printing, a brushing method, etc. are mentioned, for example. Under the present circumstances, as a raw material used, a paste is usually used, and this can adjust suitably operating rates, anode raw material particle size, etc. of a raw material, such as anode raw material fine particles, grain, a binder, a dispersant, and a pore forming material, and can prepare them by mixing.

[0014] moreover, as a solid oxide fuel cell which used the anode of this invention effectively It has two sorts of external terminals which established each material gas path in the cel and one side which prepared the cathode and the anode in both sides of a solid electrolyte, respectively. The unit cell which accumulated these, and changed or prepared the cathode and the anode in both sides of a solid electrolyte, respectively, In the solid oxide fuel cell which is equipped with the external terminal which established each material gas path in both sides at the vertical end of the direction of a laminating of a unit cell at the separator and one side which prepared each material gas path in the crossover direction mutually, respectively, accumulates these, and changes The thing using the anode of this invention as an anode is mentioned. The thing of the stack structure which arranged the external manifold also especially in such a solid oxide fuel cell is desirable.

[0015]

[Embodiment of the Invention] The expansion explanatory view of the accumulation format is shown in drawing 1 about the thing of the 3 steps of plate-like serial cel as one example of the solid oxide fuel cell of this invention. According to this, the laminating of the unit cell and separator 4 which formed the cathode 2 and this invention anode 3 in both sides of a solid electrolyte 1, respectively can be carried out by turns, and a desired accumulation cel can be produced by carrying out laminating arrangement of the external terminal 5, respectively to the unit cell of the both ends.

[0016] In order to operate such a solid oxide fuel cell, it is good to supply this to a fuel gas path almost equally, using a hydrocarbon as fuel gas. As a hydrocarbon, methane, ethane, a propane, butane, LNG, etc. are mentioned, for example. Fuel gas is preferably good a steam and to supply with nitrogen gas if needed further because of steam reforming. Moreover, the rate of flow of the fuel gas in the anode at the time of operation is preferably good to control also by in $0.05 \sim 2$ m/sec in the range of $0.05 \sim 1$ m/sec especially more preferably 0.05 to 5 m/sec. Since the rate of reforming falls, the shape of a quirk of a separator is made shallow, or the one where the rate of flow is larger can increase the rate of flow by making it thin or introducing inert gas, and can reduce the rate of reforming.

[0017]

[Effect of the Invention] The anode of this invention is suitable as an object for solid oxide fuel cells, and, as for the solid oxide fuel cell of this invention using this, the variation in the temperature distribution within a cel side is improved. Furthermore, especially since that whose specific surface area in the part which touches a solid electrolyte is $0.5 \sim 2.0 \text{ m}^2/\text{g}$ as an anode of this invention is excellent in the whole cel engine-performance balance, it is desirable. Moreover, according to the operating method of this invention, the variation in the temperature distribution in a cel side is improved, and a battery life can be maintained for a long period of time.

[0018]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

it is shown in example 1 drawing 2 -- as -- a zirconia -- yttria -- eight-mol % -- the fuel electrode was formed in one side of the solid electrolyte plate of 15cm angle which consists of doped yttria stabilized zirconia (henceforth 8YSZ) as follows. The whole surface product of a fuel electrode is bisected to every [2 / 1]. About a part for the fuel gas entrance side of them the cermet of the weight ratio 1:1 of nickel and a zirconia The powder (specific-surface-area $0.01 \text{ m}^2/\text{g}$) is put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose). Moreover, about a part for a fuel gas outlet side, the powder (specific-surface-area $0.7 \text{ m}^2/\text{g}$) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and the cermet of the weight ratio 1:1 of nickel and a zirconia was formed in 95 micrometers in thickness, respectively. Moreover, the powder (5 micrometers of mean diameters) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and LaMnO_3 was made into the air pole with a thickness of 95

micrometers at one side of another side of a solid electrolyte plate.

[0019] As shown in example 2 drawing 3 , the fuel electrode was formed in one side of the solid electrolyte plate of 15cm angle which consists of 8YSZ as follows. The whole surface product of a fuel electrode is bisected to every [2 / 1]. About a part for the fuel gas entrance side of them the cermet of the weight ratio 1:1 of nickel and a zirconia Put the powder (specific-surface-area 0.7m²/g) by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and it forms in 30 micrometers in thickness. Subsequently, the powder (specific-surface-area 0.01m²/g) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and the cermet of the weight ratio 1:1 of nickel and a zirconia was formed in 65 micrometers in thickness. About a part for a fuel gas outlet side, the powder (specific-surface-area 0.7m²/g) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and the cermet of the weight ratio 1:1 of nickel and a zirconia was formed in 95 micrometers in thickness. Moreover, the powder (5 micrometers of mean diameters) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and LaMnO₃ was made into the air pole with a thickness of 95 micrometers at one side of another side of a solid electrolyte plate.

[0020] As shown in example 3 drawing 4 , the fuel electrode was formed in one side of the solid electrolyte plate of 15cm angle which consists of 8YSZ as follows. The fuel electrode has two-layer structure. Further an eye on the whole surface the cermet of the weight ratio 1:1 of nickel and a zirconia Put the powder (specific-surface-area 0.7m²/g) by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and it forms in 90 micrometers in thickness. A bilayer eye only about a part for the fuel gas entrance side which hits one half of whole surface products the cermet of the weight ratio 1:1 of nickel and a zirconia The powder (specific-surface-area 0.01m²/g) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and it formed in 10 micrometers in thickness. Moreover, the powder (5 micrometers of mean diameters) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and LaMnO₃ was made into the air pole with a thickness of 95 micrometers at one side of another side of a solid electrolyte plate.

[0021] As shown in example of comparison 1 drawing 5 , it covered by the applying method using the coating liquid which distributed the cermet of the weight ratio 1:1 of nickel and a zirconia on one side of the solid electrolyte plate of 15cm angle which consists of 8YSZ, and distributed the powder (specific-surface-area 0.7m²/g) to the organic system binder (ethyl cellulose), and considered as the fuel electrode with a thickness of 95 micrometers. Moreover, the powder (5 micrometers of mean diameters) was put by the applying method using the coating liquid distributed to the organic system binder (ethyl cellulose), and LaMnO₃ was made into the air pole with a thickness of 95 micrometers at one side of another side of a solid electrolyte plate.

[0022] As shown in example of comparison 2 drawing 6 , the fuel electrode and the air pole

were formed in both sides of a solid electrolyte plate like the example 1 of a comparison, respectively except having replaced with the cermet of the example 1 of a comparison, and having used the cermet powder (specific surface area 0.01m²/g) of the weight ratio 1:1 of nickel and a zirconia.

[0023] Two sorts of terminal assemblies of the same magnitude as the solid electrolyte plate with an electrode and it which were obtained in example 4 example 1 thru/or the example 3 were accumulated, and the solid oxide fuel cell was produced. Each terminal assembly consisted of charge collectors which consist of La_{0.8}Sr_{0.2}CrO₃ arranged so that the slot which passes a fuel and air may intersect perpendicularly mutually at the time of accumulation, respectively. Thus, the produced fuel cell was heated. Nitrogen gas was passed, in order that a room temperature to 350 degrees C might prevent heating air and 350 to 1000 degrees C might prevent anodic oxidation to a fuel side. [a sink and] Then, it held at 10 degrees C, and hydrogen was supplied to the anode side, air was supplied to the cathode side, respectively, and the sink generation of electrical energy was started for the current with the current density of 0.3 A/cm². The result of having measured the temperature distribution within the fuel cell side at the time of a generation of electrical energy is shown in drawing 7 . As shown in drawing, generation of heat according [the temperature within a field] to a generation of electrical energy and the heat dissipation from a cel front face show that a part with high temperature is made a little to the outlet twist of gas near a center. Next, methane was supplied with the steam and the generation of electrical energy with the same current density was performed to the fuel electrode side of this cel. The ratio of methane and a steam was set up so that a steam/carbon rate might be set to 3. The temperature distribution within the fuel cell side at this time are shown in drawing 8 . This result is guessed as follows. That is, reforming of the methane is carried out to hydrogen, a steam, a carbon monoxide, and a carbon dioxide by the cermet of the nickel which is a fuel electrode ingredient, and a zirconia. Since this reforming reaction is endothermic reaction, it absorbs the heat generated by generation of electrical energy, and reduces the temperature within a fuel cell side. Furthermore, in order that reforming reaction rates may differ since the specific surface area of the fuel electrode of an entrance side and an outlet side differs, and the reaction in an outlet side may tend to progress, the temperature rise of the outlet side to which temperature tends to rise is controlled.

[0024] The generation of electrical energy trial was performed like the example 1 except having replaced the solid electrolyte plate with example of comparison 3 electrode with what was obtained in the example 1 of a comparison. The temperature distribution within the fuel cell side at this time are shown in drawing 9 . From this, the temperature near the inlet port of fuel gas is low. This shows that methane reforming happened only at the entrance and has lowered the temperature of the neighborhood.

[0025] The generation of electrical energy trial was performed like the example 1 except having replaced the solid electrolyte plate with example of comparison 4 electrode with what was obtained in the example 2 of a comparison. The temperature distribution within the fuel cell side at this time are shown in drawing 10 . It turns out that there is less

effectiveness of the temperature fall by reforming than this.

[0026] The result of having carried out continuous running of the cel by these generation-of-electrical-energy trials is shown in drawing 11 . Among drawing, even if a continuous line uses an example 1 thru/or which solid electrolyte plate with an anode of 3 in the continuous-running property in the case of an example 4, it shows the same result. Since a dotted line is a continuous-running property in the case of the example 3 of a comparison, and the example 4 of a comparison and various temperature distributions arise in a field to operation stabilized over long duration being possible, if it operates for a long time, stability will fall, and it turns out that the cell engine performance deteriorates.

[0027] As mentioned above, by changing specific surface area in the part of a fuel gas entrance side and the part of a fuel gas outlet side shows changing effectiveness about the anode surface section.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The expansion explanatory view of the accumulation format of one example of the solid oxide fuel cell of this invention.

[Drawing 2] The sectional view of one example of the solid electrolyte plate with an electrode on which the anode of this invention was made to put.

[Drawing 3] The sectional view of another example of the solid electrolyte plate with an electrode on which the anode of this invention was made to put.

[Drawing 4] The sectional view of still more nearly another example of the solid electrolyte plate with an electrode on which the anode of this invention was made to put.

[Drawing 5] The sectional view of one example of the solid electrolyte plate with an electrode on which the conventional anode was made to put.

[Drawing 6] The sectional view of another example of the solid electrolyte plate with an electrode on which the conventional anode was made to put.

[Drawing 7] The isothermal chart showing distribution whenever [cel side internal temperature / at the time of operation of the cel of this invention which used hydrogen for fuel gas].

[Drawing 8] The isothermal chart showing distribution whenever [cel side internal temperature / at the time of operation of the cel of this invention which used methane for fuel gas].

[Drawing 9] The isothermal chart showing distribution whenever [cel side internal temperature / at the time of operation of the cel of the example 3 of a comparison].

[Drawing 10] The isothermal chart showing distribution whenever [cel side internal temperature / at the time of operation of the cel of the example 4 of a comparison].

[Drawing 11] The graph which shows the continuous-running result of the cel of this invention, and the cel of the examples 3 and 4 of a comparison.

[Description of Notations]

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1 Solid Electrolyte Plate

2 Cathode

3 Anode

4 Separator

5 External Terminal

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(71) 出願人 390022998
東燃株式会社
東京都千代田区一ツ橋1丁目1番1号

(71) 出願人 590000455
財団法人石油産業活性化センター
東京都港区虎ノ門四丁目3番9号

(72) 発明者 安藤 基朗
埼玉県入間郡大井町西鶴ヶ岡一丁目3番1号
東燃株式会社総合研究所内

(72) 発明者 小出 秀人
埼玉県入間郡大井町西鶴ヶ岡一丁目3番1号
東燃株式会社総合研究所内

(74) 代理人 弁理士 河備 健二 (外2名)

最終頁に続く

(54) 【発明の名称】 固体電解質型燃料電池用アノード、それを用いた固体電解質型燃料電池及び固体電解質型燃料電池の
運転方法

(57) 【要約】

【課題】 電池の面内での温度分布のバラツキを改善し、電池寿命を長期間維持する。

【解決手段】 固体電解質型燃料電池用アノードにおいて、少なくとも燃料ガスと接触する表面部について、その材料を、燃料ガスの改質反応の触媒作用を示し、かつその比表面積について燃料ガス入口側の箇所よりも燃料ガス出口側の箇所の方を大きくしたものとする。

【特許請求の範囲】

【請求項1】 固体電解質型燃料電池用アノードにおける少なくとも燃料ガスと接触する表面部について、その材料として燃料ガスの改質反応の触媒作用を示し、かつその比表面積について燃料ガス入口側の箇所よりも燃料ガス出口側の箇所の方を大きくしたものをを用いたことを特徴とする固体電解質型燃料電池用アノード。

【請求項2】 固体電解質の両面にそれぞれカソード及びアノードを設けたセル及び片面に各原料ガス通路を設けた2種の外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして請求項1記載のアノードを用いたことを特徴とする固体電解質型燃料電池。

【請求項3】 固体電解質の両面にそれぞれカソード及びアノードを設けた単位セル、両面にそれぞれ各原料ガス通路を互いに交差方向に設けたセパレータ及び片面に各原料ガス通路を単位セルの積層方向の上下末端に設けた外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして請求項1記載のアノードを用いたことを特徴とする固体電解質型燃料電池。

【請求項4】 燃料ガスとして、炭化水素を用い、これを水蒸気とともに燃料ガス通路へ均等に供給することを特徴とする請求項2又は3記載の固体電解質型燃料電池の運転方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体電解質型燃料電池の面内での温度分布のバラツキを改善し、電池寿命を長期間維持しうる固体電解質型燃料電池用アノード、それを用いた固体電解質型燃料電池及び該電池の運転方法に関するものである。

【0002】

【従来の技術】燃料電池において、メタンなどの炭化水素を燃料ガスに用い、水蒸気改質などの改質反応により燃料ガスを水素等に変換させ、これを実質的な燃料ガスとして利用することが広く行われているが、このようなものを含め、一般に大型化した燃料電池はセル面内の温度分布の上下幅が大きいという問題があった。すなわち、燃料電池の作動時において、通常燃料ガスはセルの各供給部分に均等に供給、分配されているが、その場合、セル面内の温度分布は、燃料ガスの流路についてみると入り口側の方が低温、出口側の方が高温であり、しかも燃料ガス及び空気などの酸化剤ガスの各流路の出口寄りの交差部付近が最高温となる。このような温度分布のバラツキのため、低温部では電池性能の低下が生じ、また高温部では腐食などが進行しやすく電池寿命を長期間維持するのが困難となり、特に大型のスタック構造のものでは深刻な問題となる。このため、冷却ユニットを数セルごとに挟むなどの措置がなされているが、部材点数が多くなり、コスト高となるのを免れなかった。

【0003】このため、熔融炭酸塩型燃料電池、なかなか直接内部改質式のものにおいては、セル面内の温度分布の制御を改質触媒の充填密度を最適化することなどで行っている。この直接内部改質式のものは、一般に、熔融炭酸塩型燃料電池が、それに供給する燃料の改質方式により、改質装置を燃料電池本体とは別に設ける外部改質方式と、電池内部で燃料を改質する内部改質方式とに大別され、特に後者はシステムの小型化、発電効率の向上などの点で優れているが、この内部改質方式の中で有望視されている、燃料電池本体の燃料ガス通路内に改質触媒を配置する方式のものである。

【0004】他方、固体電解質型燃料電池においては、前記熔融炭酸塩型燃料電池のように改質触媒が電極材料とは別に配置されるのではなく、アノードがそのまま改質触媒として作用し、改質反応は速い反応速度で主に燃料ガスと接するアノード表面上で起こる。このため、改質反応は燃料ガス流路入り口側に偏って起こり、中でも水蒸気改質反応を利用する場合には、該反応が吸熱反応であるため、燃料ガス流路入り口側のセル面において急激な温度低下を招き、セル面内の温度分布が一層拡大するのを免れず、さらに、熱応力による歪が不均一に発生するため、この温度分布の制御が強く要望されていた。

【0005】

【発明が解決しようとする課題】本発明は、このような事情の下、温度分布のバラツキを改善し、電池寿命を長期間維持しうる固体電解質型燃料電池用アノードを提供するとともに、該アノードを有効に利用した、所定固体電解質型燃料電池及び該電池の運転方法を提供することを目的となされたものである。

【0006】

【課題を解決するための手段】本発明者らは、前記した好ましい特性を有する固体電解質型燃料電池用アノードを開発すべく、鋭意研究を重ねた結果、先に改質触媒能をもつアノードの燃料ガスとの接触面のうち、燃料ガス入口側の箇所に、改質反応の触媒作用を示さないセラミックスからなる所定厚さ、所定孔径のガス透過性多孔質層を設けた所定燃料電池用アノードを提案した（特願平7-92500号）。このアノードは、水蒸気改質反応などの改質反応を燃料ガス入口側に集中して偏らせることなく、それより下流側へも広げて行わせ、改質反応の起こる箇所の中心部を下流側へシフトさせてセル面内の温度分布を制御するようにしたものである。本発明者らは、さらに研究を重ねた結果、このアノードのように反応箇所を偏らせないため別の被覆層を設けることなく、改質触媒能をもつアノード材料、中でも同質素材、例えば均一組成のサーメットなどの該アノード材料のみで形成し、かつアノードの少なくとも燃料ガスとの接触表面部の比表面積についてその燃料ガス入口側よりも燃料ガス出口側の方を大きくすることにより、このアノードを用いたセルにおいて、長期間にわたりセル面内の温度分

布を十分制御することができ、セル性能を長期間安定に維持しうることを見出し、この知見に基づいて本発明をなすに至った。

【0007】すなわち、本発明は、(1) 固体電解質型燃料電池用アノードにおける少なくとも燃料ガスと接触する表面部について、その材料として燃料ガスの改質反応の触媒作用を示し、かつその比表面積について燃料ガス入口側の箇所よりも燃料ガス出口側の箇所の方を大きくしたものをを用いたことを特徴とする固体電解質型燃料電池用アノード、(2) 固体電解質の両面にそれぞれカソード及びアノードを設けたセル及び片面に各原料ガス通路を設けた2種の外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして前記(1)項記載のアノードを用いたことを特徴とする固体電解質型燃料電池、(3) 固体電解質の両面にそれぞれカソード及びアノードを設けた単位セル、両面にそれぞれ各原料ガス通路を互いに交差方向に設けたセパレータ及び片面に各原料ガス通路を単位セルの積層方向の上下末端に設けた外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして前記(1)項記載のアノードを用いたことを特徴とする固体電解質型燃料電池、及び(4) 燃料ガスとして、炭化水素を用い、これを水蒸気とともに燃料ガス通路へ均等に供給することを特徴とする前記(2)項又は

(3)項記載の固体電解質型燃料電池の運転方法を提供するものである。本発明の好ましい態様としては、

(5) アノードがニッケル、酸化ニッケル及びニッケルとセラミックスのサーメットの中から選ばれた少なくとも1種である前記(1)項記載のアノード、(6) 比表面積が、燃料ガス入口側の箇所で $0.01 \sim 0.2 \text{ m}^2/\text{g}$ 、燃料ガス出口側の箇所で $0.5 \sim 2.0 \text{ m}^2/\text{g}$ である前記(1)項記載のアノード、(7) セラミックスがジルコニア、安定化ジルコニア、セリア、アルミナ、窒化ケイ素及びその他酸素分圧 $1 \times 10^{-20} \text{ atm}$ の雰囲気下 1200°C で溶融しないセラミックスの中から選ばれた少なくとも1種である前記(5)項又は

(6)項記載のアノード、(8) サーメットがニッケルとジルコニアのサーメット又はニッケルとセリアのサーメットである前記(5)項、(6)項又は(7)項記載のアノード、(9) 固体電解質の両面にそれぞれカソード及び改質触媒能をもつアノードを設けた単位セル、両面にそれぞれ各原料ガス通路を互いに交差方向に設けたセパレータ及び片面に各原料ガス通路をセパレータの各原料ガス通路と同様に設けた外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして前記(5)項ないし(8)項のいずれかに記載のアノードを用いたことを特徴とする固体電解質型燃料電池、が挙げられる。最も好ましいアノードの態様としては、(10) アノードと固体電解質との界面付近のアノード部位が $0.5 \sim 2.0 \text{ m}^2/\text{g}$ の比表面積

を有する前記(1)項、(5)項、(6)項、(7)項及び(8)項のいずれかに記載のアノード、が挙げられる。

【0008】本発明のアノードにおいては、少なくとも燃料ガスと接触する表面部、好ましくはこの表面部に限らずアノード全体が燃料ガスの改質反応の触媒作用を示す材料からなる。この材料は同質素材、例えば均一組成のサーメットなどであるのが好ましい。

【0009】このアノード材料については、燃料ガス、特に炭化水素の改質反応の触媒作用を示すもの、すなわち改質触媒能をもつものであれば特に制限されないが、好ましくはメタン、エタン、プロパン、ブタン、LNG等の炭化水素の改質反応、特に水蒸気改質反応の触媒作用を示すもの、例えばニッケル、酸化ニッケル及びニッケルとセラミックスのサーメットの中から選ばれた少なくとも1種などが挙げられる。

【0010】上記サーメットを構成するセラミックスとしては、ジルコニア、イットリア安定化ジルコニア(以下、YSZという)などの安定化ジルコニア、セリア、アルミナ、窒化ケイ素、その他酸素分圧 $1 \times 10^{-20} \text{ atm}$ の雰囲気下 1200°C で溶融しないセラミックスなどが挙げられる。

【0011】上記サーメットとしては、好ましくは、ニッケル-ジルコニア、酸化ニッケル-ジルコニア、ニッケル-セリア、酸化ニッケル-セリア、ニッケル-YSZ、酸化ニッケル-YSZが挙げられる。

【0012】本発明のアノードの前記表面部について、その材料の比表面積は、燃料ガス入口側の箇所よりも燃料ガス出口側の箇所の方を大きくすることが必要であ

る。この比表面積は、燃料ガス入口側の箇所において好ましくは $0.01 \sim 0.2 \text{ m}^2/\text{g}$ 、より好ましくは $0.01 \sim 0.1 \text{ m}^2/\text{g}$ 、燃料ガス出口側の箇所において好ましくは $0.5 \sim 2.0 \text{ m}^2/\text{g}$ 、より好ましくは $0.5 \sim 1.0 \text{ m}^2/\text{g}$ の範囲で選ばれる。また、本発明のアノードの形態としては、例えばこの表面部を適当な比率、例えば $1/2$ ずつに二分し、その一方の燃料ガス入口側分と他方の燃料ガス出口側分とでその材料の比表面積について上記のように変えたものなどが挙げられるが、好ましくは、表面部に限らずアノード全体を適当な比率に二分し、その燃料ガス出口側分については単層とするとともに、燃料ガス入口側分については2層構造、例えば燃料ガス出口側分と全く同じ下層とそれに比し比表面積が小さい上層との積層構造などとするのがよい。また、アノードと固体電解質との界面付近のアノード部位、中でもアノードの固体電解質と接する部位における比表面積の多寡は端的に電極活性ひいては分極抵抗などに影響するため、この比表面積は大きい方が好ましいが、アノード全体を他の部材と共に組み込んだ電池全体としては、全体的にバランスのよいセル性能、すなわち変換効率、出力密度、耐久性、安定性などの総合パラ

ンスの優れたセル性能が要求されるため、この比表面積として好適なのは0.5~2.0 m²/gの範囲である。

【0013】本発明のアノードの固体電解質への被着方法としては、例えばスクリーン印刷法、はけ塗り法などが挙げられる。この際用いられる原料としては、通常ペーストが用いられ、これはアノード原料粉体や粒体、バインダー、分散剤、増孔剤などの原材料の使用割合やアノード原料粒径等を適宜調整して、混合することによって調製することができる。

【0014】また、本発明のアノードを有効に利用した固体電解質型燃料電池としては、固体電解質の両面にそれぞれカソード及びアノードを設けたセル及び片面に各原料ガス通路を設けた2種の外部端子を備え、これらを集積して成るか、あるいは固体電解質の両面にそれぞれカソード及びアノードを設けた単位セル、両面にそれぞれ各原料ガス通路を互いに交差方向に設けたセパレータ及び片面に各原料ガス通路を単位セルの積層方向の上下末端に設けた外部端子を備え、これらを集積して成る固体電解質型燃料電池において、アノードとして本発明の

【0015】

【発明の実施の形態】図1に、本発明の固体電解質型燃料電池の1例としての平板状3段直列セルのものについて、その集積様式の展開説明図を示す。これに従い、固体電解質1の両面にそれぞれカソード2及び本発明アノード3を設けた単位セルとセパレータ4とを交互に積層し、その両端の単位セルにそれぞれ外部端子5を積層配設することによって所望の集積セルを作製することができる。

【0016】このような固体電解質型燃料電池を運転するには、燃料ガスとして、炭化水素を用い、これを燃料ガス通路へほぼ均等に供給するのがよい。炭化水素としては、例えばメタン、エタン、プロパン、ブタン、LNGなどが挙げられる。燃料ガスは、好ましくは水蒸気改質のため水蒸気、さらには必要に応じ窒素ガスとともに、供給するのがよい。また、運転時のアノードにおける燃料ガスの流速は、好ましくは0.05~5 m/sec、より好ましくは0.05~2 m/sec、中でも特に0.05~1 m/secの範囲に制御するのがよい。流速は大きい方が改質率が低下するので、セパレータの溝形状を浅くしたり、細くするか、あるいは不活性ガスを導入することで流速を増大させて改質率を低下させることができる。

【0017】

【発明の効果】本発明のアノードは、固体電解質型燃料電池用として好適であり、これを用いた本発明の固体電解質型燃料電池は、セル面内の温度分布のバラツキが改

善される。さらに、本発明のアノードとしては、固体電解質と接する部位における比表面積が0.5~2.0 m²/gのものが、セル性能の全体バランスに優れるので特に好ましい。また、本発明の運転方法によれば、セル面内での温度分布のバラツキを改善し、電池寿命を長期間維持しうる。

【0018】

【実施例】次に実施例によって本発明をさらに詳細に説明するが、本発明はこれらの例によって何ら限定されるものではない。

実施例1

図2に示すように、ジルコニアにイットリアを8モル%ドープしたイットリア安定化ジルコニア（以下、8YSZという）からなる15cm角の固体電解質板の片面に、次のようにして燃料極を形成した。燃料極の全面積を1/2ずつに二分し、そのうちの燃料ガス入口側分についてはニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.01 m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着し、また燃料ガス出口側分についてはニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.7 m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着し、それぞれ厚さ95 μmに形成した。また、固体電解質板の他方の片面には、LaMnO₃を、その粉末（平均粒径5 μm）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着し厚さ95 μmの空気極とした。

【0019】実施例2

図3に示すように、8YSZからなる15cm角の固体電解質板の片面に、次のようにして燃料極を形成した。燃料極の全面積を1/2ずつに二分し、そのうちの燃料ガス入口側分についてはニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.7 m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ30 μmに形成し、次いでニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.01 m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ65 μmに形成した。燃料ガス出口側分についてはニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.7 m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ95 μmに形成した。また、固体電解質板の他方の片面には、LaMnO₃を、その粉末（平均粒径5 μm）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着し厚さ95 μmの空気極とした。

【0020】実施例3

図4に示すように、8YSZからなる15cm角の固体電解質板の片面に、次のようにして燃料極を形成した。燃料極は2層構造になっており、一層目は全面にニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.7m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ90μmに形成し、二層目は全面積の1/2に当たる燃料ガス入口側分についてのみニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.01m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ10μmに形成した。また、固体電解質板の他方の片面には、LaMnO₃を、その粉末（平均粒径5μm）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着し厚さ95μmの空気極とした。

【0021】比較例1

図5に示すように、8YSZからなる15cm角の固体電解質板の片面に、ニッケルとジルコニアの重量比1:1のサーメットを、その粉末（比表面積0.7m²/g）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ95μmの燃料極とした。また、固体電解質板の他方の片面には、LaMnO₃を、その粉末（平均粒径5μm）を有機系バインダー（エチルセルロース）に分散した塗布液を用いた塗布法により被着して厚さ95μmの空気極とした。

【0022】比較例2

図6に示すように、比較例1のサーメットに代えてニッケルとジルコニアの重量比1:1のサーメット粉末（比表面積0.01m²/g）を用いた以外は比較例1と同様にして固体電解質板の両面にそれぞれ燃料極及び空気極を形成した。

【0023】実施例4

実施例1ないし実施例3で得られた電極付き固体電解質板とそれと同じ大きさの2種の端子板とを集積し、固体電解質型燃料電池を作製した。各端子板はそれぞれ燃料及び空気を流す溝が集積時に互いに直交するように配設されるLa_{0.8}Sr_{0.2}CrO₃から成る集電体で構成した。このようにして作製した燃料電池を加熱した。室温から350℃までは加熱空気を流し、350℃から1000℃までは燃料側にアノード酸化を防止するために窒素ガスを流した。その後、10℃に保持してアノード側に水素、カソード側に空気をそれぞれ供給し、0.3A/cm²の電流密度で電流を流し発電を開始した。発電時の燃料電池面内の温度分布を測定した結果を図7に示す。図のように面内の温度は発電による発熱とセル表面からの放熱により、中央付近でややガスの出口より温度の高い部分がでることが分る。次に、このセルの燃料極側にメタンガスを水蒸気とともに供給し同じ電流密

度での発電を行った。メタンガスと水蒸気の比率は水蒸気/炭素比が3になるように設定した。このときの燃料電池面内の温度分布を図8に示す。この結果は、次のように推測される。すなわち、メタンガスは燃料極材料であるニッケルとジルコニアのサーメットにより水素、水蒸気、一酸化炭素、二酸化炭素に改質される。この改質反応は吸熱反応であるため、発電によって発生する熱を吸収し、燃料電池面内の温度を低下させる。また、さらに入口側、出口側の燃料極の比表面積が異なるため改質反応速度が異なり、出口側での反応が進みやすいため、温度が上昇しやすい出口側の温度上昇が抑制される。

【0024】比較例3

電極付き固体電解質板を比較例1で得られたものに代えた以外は実施例1と同様にして発電試験を行った。このときの燃料電池面内の温度分布を図9に示す。これより、燃料ガスの入口付近の温度が低くなっている。これは、メタン改質が入口だけで起こり、その付近の温度を下げていることを示すものである。

【0025】比較例4

電極付き固体電解質板を比較例2で得られたものに代えた以外は実施例1と同様にして発電試験を行った。このときの燃料電池面内の温度分布を図10に示す。これより、改質による温度低下の効果が少ないことが分る。

【0026】これらの発電試験でセルを連続運転した結果を図11に示す。図中、実線は実施例4の場合の連続運転特性で実施例1ないし3のいずれのアノード付き固体電解質板を用いても同様の結果を示し、長時間にわたって安定した運転が可能であるのに対し、点線は比較例3及び比較例4の場合の連続運転特性であって、面内に多様な温度分布が生じるために、運転を長時間行くと安定性が低下し、電池性能が劣化することが分る。

【0027】以上のように、アノード表面部について、燃料ガス入口側の箇所と燃料ガス出口側の箇所とで比表面積を変えることにより、効果が変動することが分る。

【図面の簡単な説明】

【図1】 本発明の固体電解質型燃料電池の1例の集積様式の展開説明図。

【図2】 本発明のアノードを被着させた電極付き固体電解質板の1例の断面図。

【図3】 本発明のアノードを被着させた電極付き固体電解質板の別の例の断面図。

【図4】 本発明のアノードを被着させた電極付き固体電解質板のさらに別の例の断面図。

【図5】 従来のアノードを被着させた電極付き固体電解質板の1例の断面図。

【図6】 従来のアノードを被着させた電極付き固体電解質板の別の例の断面図。

【図7】 水素を燃料ガスに用いた、本発明のセルの運転時のセル面内温度分布を示す等温図。

【図8】 メタンを燃料ガスに用いた、本発明のセルの

運転時のセル面内温度分布を示す等温図。

【図 9】 比較例 3 のセルの運転時のセル面内温度分布を示す等温図。

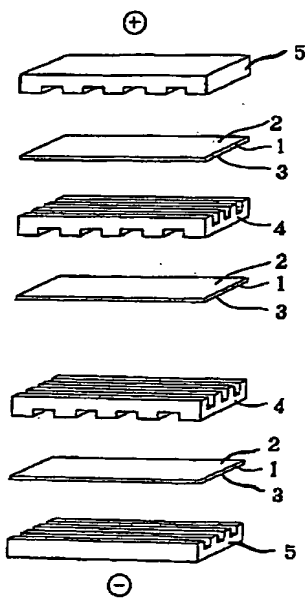
【図 10】 比較例 4 のセルの運転時のセル面内温度分布を示す等温図。

【図 11】 本発明のセルと比較例 3 及び 4 のセルの連続運転結果を示すグラフ。

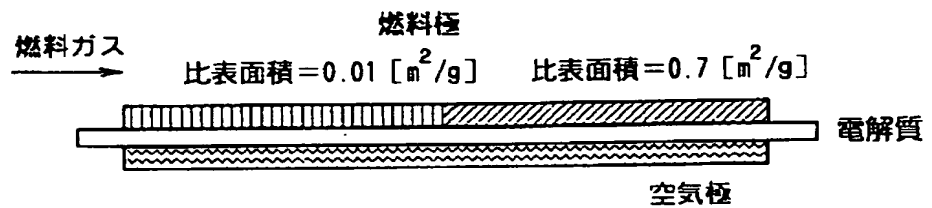
【符号の説明】

- 1 固体電解質板
- 2 カソード
- 3 アノード
- 4 セパレータ
- 5 外部端子

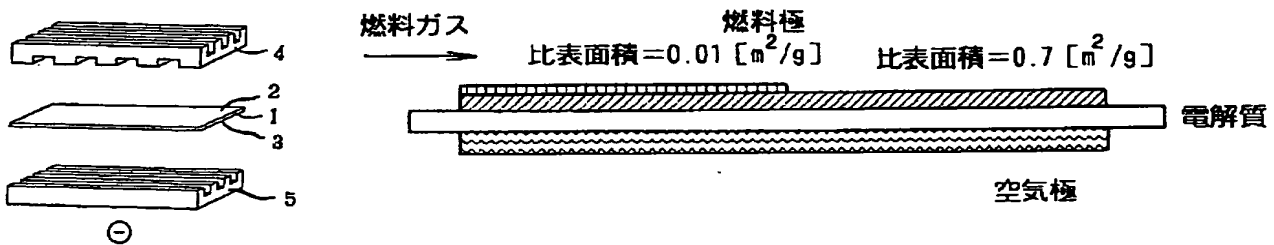
【図 1】



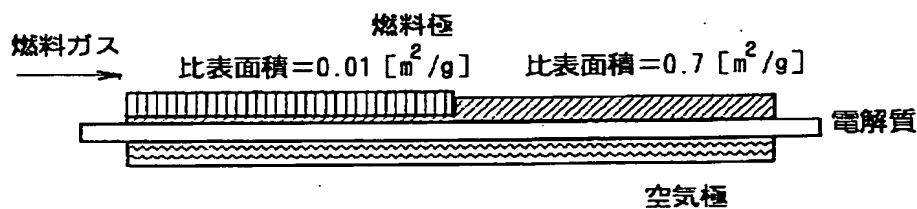
【図 2】



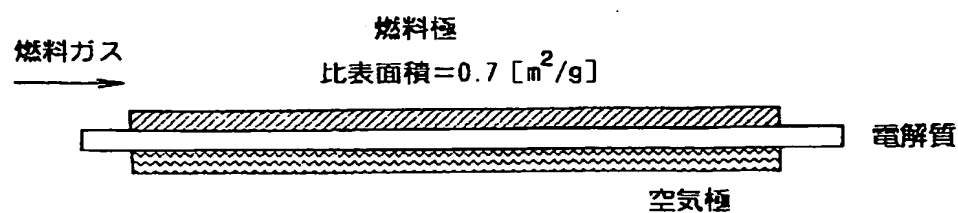
【図 4】



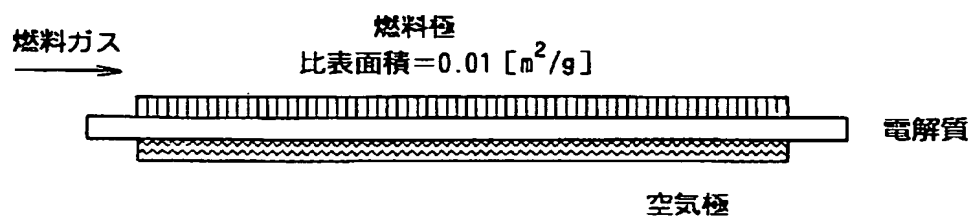
【図 3】



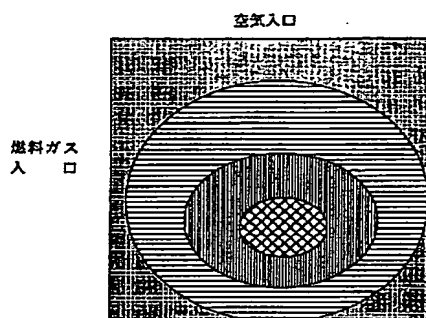
【図 5】



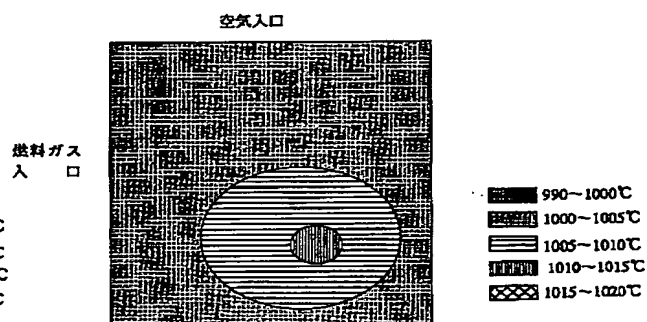
【図 6】



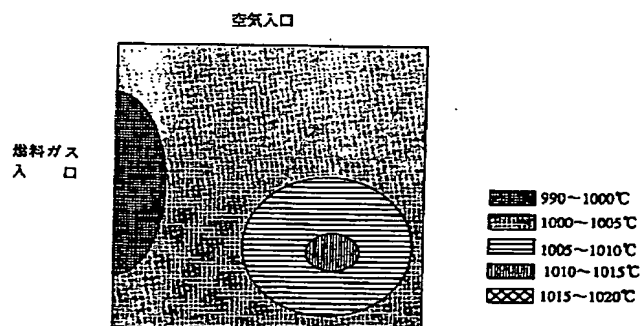
【図 7】



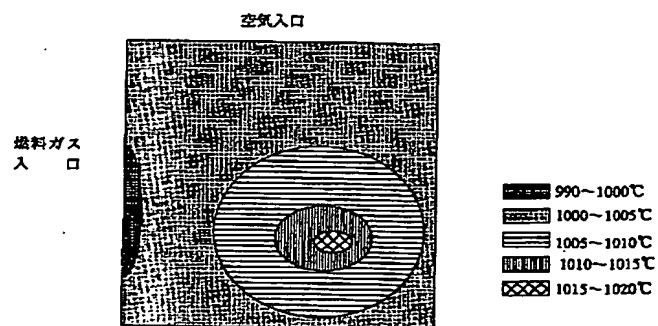
【図 8】



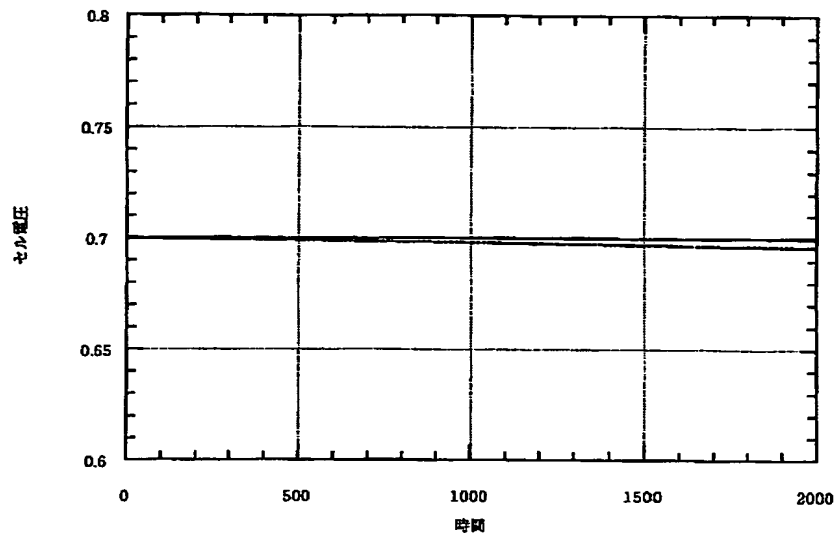
【図 9】



【図 10】



【図 1 1】



フロントページの続き

(72)発明者 染谷 喜幸
埼玉県入間郡大井町西鶴ヶ岡一丁目3番1
号 東燃株式会社総合研究所内

(72)発明者 向沢 功
埼玉県入間郡大井町西鶴ヶ岡一丁目3番1
号 東燃株式会社総合研究所内
(72)発明者 吉田 利彦
埼玉県入間郡大井町西鶴ヶ岡一丁目3番1
号 東燃株式会社総合研究所内

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